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ACIDIFICATION OF FOREST SOILS: MODEL DEVELOPMENT AND APPLICATION FOR ANALYZING IMPACTS OF ACIDIC DEPOSITION IN EUROPE

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ABSTRACT

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Acidification is considered to be an unfavourable process in forest soil. Timber logging, natural accumulation of biomass in the ecosystem, and acidic deposition are known sources of acidification. Acidification causes a risk of damage to plant roots and subsequent risk of a decline in ecosystem productivity.

A dynamic model is introduced for describing the acidification of forest soils. In 1-year time steps the model calculates the soil pH as a function of the acid stress and the buffer mechanisms of the soil. Acid stress is defined as the hydrogen ion input into the top soil. The buffer mechanisms counteract acidification by providing a sink for hydrogen ions. The concepts *buffer rate* and *buffer capacity* are used to quantify the buffer mechanisms. The model compares (a) the rate of acid stress (annual amount) with the buffer rate, and (b) the accumulated acid stress (over several years) with the buffer capacity. These two comparisons give an estimate of the soil acidity.

The model was incorporated into the Regional Acidification INformation and Simulation (RAINS) model system of the International Institute for Applied Systems Analysis for analyzing the acidic deposition problem in Europe. This system links information on energy production, pollutant emission, pollutant transport, and pollutant deposition. The data on acid stress entering the soils was obtained from other submodels. Data on buffer rate and buffer capacity were collected from soil maps and geological maps.

The model system as a whole is now available for analyzing the impact of different emission scenarios. The soil acidification model assumes sulfur deposition estimates from the other submodels as input, and as output it produces estimates of the acidity of European forest soils in a map format. Additionally it computes the total area of forests in Europe with the estimated soil pH lower than any selected threshold value. Sources of uncertainty in the soil acidification model are listed and briefly evaluated.

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INTRODUCTION

Extensive forest damage has been observed in rural areas of Central Europe since the 1970's. It was first reported on silver fir (Schütt, 1977) and later on Norway spruce, Scots pine, beech, and other tree species (Schütt et al., 1983). In 1984, in the Federal Republic of Germany damage was reported for a forest area of 2 549 000 ha (Lammel, 1984). Forest damage is a result of many factors including the direct impact of air pollutants on tree foliage, soil acidification, and climate. In this study we concentrate on soil acidification, which has been demonstrated as an important link between air pollution and forest damage. It is intended that other factors contributing to the forest damage will be incorporated into the model as soon as possible.

The study includes model development and model application. The main objective of the study is to develop a method for computing the time evolution of acidification of forest soils. An additional objective is to apply the model for getting an overview of the forest soil acidification due to air pollution at the European level.

SOIL ACIDIFICATION

Soil acidification has been defined as being a decrease in the acid neutralization capacity of the soil (Van Breemen et al., 1984). Such a decrease may coincide with a decrease in soil pH. It may also take place in conditions of a relatively constant pH assuming efficient buffering processes. In such a case the buffering of the soil counteracts the effect of acidic deposition or biomass removal, so that over long periods of time the soil pH remains stable. Nevertheless the neutralization capacity is being depleted and the soil is subject to acidification.

Acid stress

Acid stress is defined as the input of hydrogen ions into the top-soil. Acid stress can result from acidic deposition of air pollutants, from biomass utilization, and from the natural biological activity of ecosystems (Ulrich, 1983a; Van Breemen et al., 1984). Any one of these sources can dominate the stream of protons entering the soil. The acid stress due to air pollution can result from the direct deposition of hydrogen ions or from the indirect effect of acid-producing substances such as the dry deposition of SO_2.

Acid stress has two important aspects. One is the accumulative load of the stress and the other is the instantaneous rate of the stress. The variable *amount of stress* refers to the load, and involves accumulation over several

years. The unit for the amount of stress is kilomoles of acidity per hectare (kmol ha^{-1}). The variable *stress rate* refers, in principle, to the time derivative of the amount of stress although in practice it is given as annual hydrogen ion input. The unit for the stress rate is kilomoles of acidity per hectare per year (kmol ha^{-1} $year^{-1}$).

Buffering processes

Soil reacts to acid stress depending on the soil properties. Acid stress implies influx of hydrogen ions, and in the corresponding way the buffering properties of the soil imply consumption of hydrogen ions. Buffering is described using two variables, one for the gross potential and the other for the rate of the reaction. Both variables refer to the intrinsic properties of the soil and can be quantified after fixing the volume of the reacting soil layer.

Buffer capacity, the gross potential, is the total reservoir of the buffering compounds in the soil. The unit for the buffer capacity is the same as that for the amount of acid stress (kmol ha^{-1}).

Buffer rate, the rate variable, is defined as the maximum potential rate of the reaction between the buffering compounds and the hydrogen ions. This variable is needed because the reaction kinetics is sometimes of importance. The buffer capacity may be high but the rate may limit the hydrogen ion consumption. Buffer rate is expressed in units which are comparable to those of the stress rate (kmol ha^{-1} $year^{-1}$).

The proton consumption reactions in soils have been systematically described by Ulrich (1981, 1983b). A consecutive series of chemical reactions has been documented for soils subject to acidification. Information regarding the dominant reactions has been used for defining categories, called *buffer ranges*. They are briefly described in the following paragraphs and summarized in Table 1. The name of each buffer range refers to the dominant buffer reaction and the typical pH ranges given refer to the pH of a soil/water suspension ($pH(H_2O)$).

Carbonate buffer range. Soils containing $CaCO_3$ in their fine earth fraction (calcareous soils) are classified into the carbonate buffer range ($pH \geqslant 6.2$). Ca^{2+} is the dominant cation in the soil solution and on the exchange surfaces of the soil particles. The buffer capacity of soils in this range is proportional to the amount of $CaCO_3$ in the soil. In a case where $CaCO_3$ is evenly distributed in the soil, the buffer rate, i.e. the dissolution rate of $CaCO_3$, is high enough to buffer any occurring rate of acid stress.

Silicate buffer range. If there is no $CaCO_3$ in the fine earth fraction and carbonic acid is the only acid being produced in the soil, the soil is classified

TABLE 1

Classification of the acid buffering reactions in forest soils (Ulrich, 1981, 1983b)

Buffer range	pH range	Base saturation	Buffer reaction
Carbonate	8.0–6.2	1.00	$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^-$
Silicate	6.2–5.0	1.00–0.70	$CaAl_2Si_2O_8 + 2H_2CO_3 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- + Al_2Si_2O_5(OH)_4$
Cation exchange	5.0–4.2	0.70–0.05	clay mineral $= Ca + 2H^+ \rightarrow$ H-clay mineral-$H + Ca^{2+}$
Aluminium	4.2–3.0	0.05–0.00	$AlOOH + 3H^+ \rightarrow Al^{3+} + 2H_2O$
Iron	< 3.8	0.00	$FeOOH + 3H^+ \rightarrow Fe^{3+} + 2H_2O$

into the silicate buffer range ($6.2 > pH \geqslant 5.0$). In this range the only buffer process acting in the soils is the weathering of silicates and the associated release of base cations, since the dissolution of aluminous compounds is not significant until a pH of less than 5.0 is reached. The buffer rate is often quite low, but the buffer capacity is high, as it is formed by the massive storage of the silicate material. The weathering of silicates occurs throughout all buffer ranges. The switch to lower buffer ranges implies that the weathering rate of silicates is not sufficient to buffer the acid stress completely.

Cation exchange buffer range. The soils are classified into the cation exchange buffer range when the cation exchange reactions play the major role in acid buffering: the silicate buffer range is inadequate to buffer the acid stress completely. The excess stress, not buffered by the reactions of the silicate buffer range, is adsorbed in the form of H^+- or Al-ions at the exchange sites, thus displacing the base cations. The cation exchange reactions are fast and, therefore, the buffer rate of soils in this range effectively counteracts any occurring rates of acid stress. The total buffer capacity ($=$ cation exchange capacity, CEC_{tot}) is generally rather low, depending mainly on the soil texture. The remaining buffer capacity at any given time is quantified by *base saturation*, the percentage of base cations of the total CEC. As long as the base saturation stays above 5–10%, the excess stress is buffered by the cation exchange reactions and the soil pH takes a value between 5.0 and 4.2, the actual value depending on the base saturation.

Aluminium buffer range. Below the critical value of base saturation the soils are classified into the aluminium buffer range. Hydrogen ions are consumed

when releasing aluminium mainly from clay minerals. These reactions merely change the form of acidity from hydrogen ions to Al^{3+}. The leachate is thus capable of acidifying adjacent ecosystems. High aluminium ion concentrations characterize the soil solution and may cause toxic effects on bacteria and plant roots. The soil pH is within the range 4.2–3.0.

Aluminium compounds are abundant in soils, so that the buffer capacity rarely restricts the reaction. Buffer rate is decisive: soils do not fall below the aluminium buffer range until the stress rate exceeds the production rate of highly dissolvable Al-hydroxy-compounds.

Iron buffer range. At the extreme stage of acidification, soils may be classified into the iron buffer range. Increasing solubility of iron oxides is observed. This leads to visible (colour) symptoms in the soil profile, which is not the case for aluminium, although in quantitative terms aluminium may still act as the dominant buffer compound. The pH-values as low as 3.0 indicate that living organisms will suffer from toxicity and nutrient deficiency.

MODEL DEVELOPMENT

Basic assumptions

The requirement of a large spatial scale necessitates several simplifications in the model. The assumptions affecting the model structure itself are briefly described here, whereas the additional assumptions included in the model application at its present stage are discussed in a subsequent chapter.

The soil is considered as a homogeneous box. It is, however, possible to divide the soil into several layers if it is considered important when estimating the effects of soil acidification. In fact, this has already been done in connection with the RAINS surface water acidification model (Kämäri et al., 1985), where two layers were introduced.

The ion exchange and buffering properties of organic matter are not taken into account separately from the inorganic buffer systems. Information on the humus content of the soil or the thickness of the moor layer is not commonly available from different parts of Europe. At least in northern Europe, where the accumulation of organic matter is significant, it would be important to take the buffering properties of organic matter into account.

The model was designed to focus on the year-to-year changes in soil acidity. Seasonal, monthly or even daily patterns of soil acidity are potentially very important as they may effectively act as key situations triggering biological effects. Our model describes the annual baseline level for the short-term peaks of low or high acidity. In this way it does not directly focus

on the potentially crucial events but it estimates trends of increasing probabilities of such events. This restriction of focus made it possible to exclude redox processes and sulphate adsorption processes from the model. It was assumed that these processes generate seasonal variability in soil acidity which levels out in the long run without affecting the year-to-year trend.

The weathering rate of silicates and the connected release of base cations is assumed to be independent of the soil pH. In some laboratory experiments it has been shown that the release of silicates increases with decreasing pH (e.g. Wollast, 1967; Busenberg and Clemency, 1975; Stumm et al., 1983). However, the release of silica does not necessarily imply that base cations are released at the same rate. They may precipitate with aluminium compounds to form clay minerals. Increased base cation leaching is usually due to cation exchange reactions, not necessarily to increased weathering rate. In Solling, Federal Republic of Germany, no deviation in the weathering rate of silicate from the long-term average has been observed, although the pH of the soil has decreased (Matzner, unpublished).

MODEL STRUCTURE

The model describes soil acidification in terms of the sequence of the buffer ranges. It compares (a) the amount of stress (cumulative value over the time period of interest) with the buffer capacity, and (b) the stress rate (year-to-year basis) with the buffer rate. The comparisons are made separately for the carbonate, silicate and cation exchange buffer ranges. The model thus assumes that values for the buffering variables – buffer capacity and buffer rate – are determined separately for each of these buffer ranges. For the aluminium and iron ranges, and equilibrium approach was chosen. The soil pH is assumed to stay in equilibrium with solid phases of aluminium compounds.

All the buffering variables do not have to be considered in the model. The buffer rates of the carbonate range and the cation exchange range are so high that in practice they cannot be exceeded by any occurring rate of acid stress. Moreover, the buffer capacities of silicate and aluminium ranges cannot be exhausted in the time scale of hundreds of years. The iron range is assumed to be quantitatively irrelevant for buffering at pH-values above 3.0. In this way the number of buffering variables actually included into the model reduces to four. The excluded variables receive values high enough not to affect the model output.

The model is used by taking the given pattern of acid stress as the input variable. The program compares the (annual) acid stress with the buffer rate determined for the prevailing buffer range. It also compares the accumulated

amount of acid stress with the buffer capacity. With these comparisons the program calculates which buffer range prevails each year, and then computes the approximation of the prevailing soil pH.

Acid stress to the top soil is partly or totally neutralized by the weathering

The Geological Map was used to determine parent materials of soils in each grid square. Depending on the dominant parent material the soil of each grid square was classified into one of the above categories.

Based on this information the model is applicable for producing acidification scenarios for forest soils. The model is run separately for each soil type within the grid square. An estimate of soil pH is the output.

Results of model runs

Two example scenarios were introduced using the IIASA energy-emission model, and the long-range transport model supplied by the EMEP program. From 1960 until 1980 the scenarios were identical. From then on the scenarios diverged so that the 'high' deposition scenario assumed high rates of energy development throughout Europe, as defined by the ECE 'trends continued' scenario (ECE, 1983) linearly extrapolated to 2030. The 'low' deposition scenario was constructed according to the ECE 'conservation' scenario, assuming lower rates of energy use and, in addition to that, effective measures taken for the control of sulfur emissions (Fig. 5). The specific method of generating different scenarios is presented elsewhere (Alcamo et al., 1985).

The model can be used for producing an estimate of the pH ranges of forest soils in Europe for any selected scenario and year (Fig. 6). An

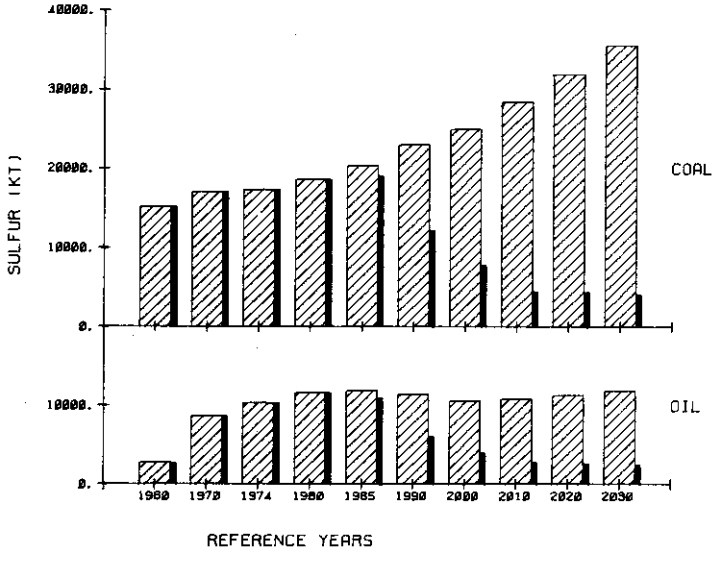

Fig. 5. Total sulfur emitted in Europe according to the 'high' and 'low' emission scenario from coal and oil sectors.

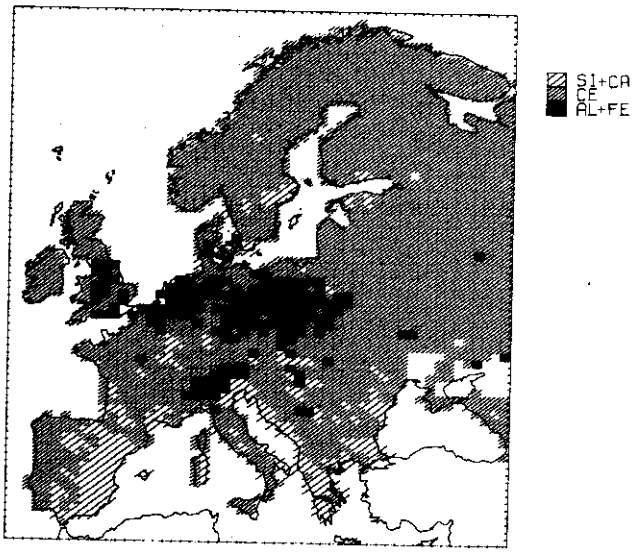

Fig. 6. Model estimates of the soil acidity in Europe in 1980. Si + Ca represent the silicate and carbonate buffer ranges, CE cation exchange buffer range, and Al + Fe aluminium and iron buffer ranges.

additional option is to display the areas with soils in a critical buffer range or areas with soils below a critical pH. This concept bears on the notion that the risk of forest damage increases below a critical acidity. A default value of 4.2 is introduced for the critical pH but the model user can interactively select other values. The area below a critical pH value can be displayed in map format, with different shadings indicating the percentage of the total forest area with soil pH below the selected value (Fig. 7).

For summarizing the results an option has been added to display estimates of the time patterns of the total forest area with soils below the critical acidity (Fig. 8). The area of the forest in each grid square is calculated and the time evolution of the area of European forests with soil pH below a selected critical value is then displayed.

As part of the IIASA study this application of the soil acidification model is designed for quick comparisons of sulfur emission scenarios. It is up to the model user to decide what kind of scenarios should be compared. The two examples were selected to demonstrate the model behaviour. Therefore, the examples are relatively useless as far as selection of feasible policy options is concerned. In the following paragraphs we will discuss the effects of the 'low' vs. the 'high' scenario but this discussion is intended merely to demonstrate the properties of the model.

By the year 1980, that is assuming the historical deposition pattern, the model predicts a decline in the soil pH over relatively large regions of

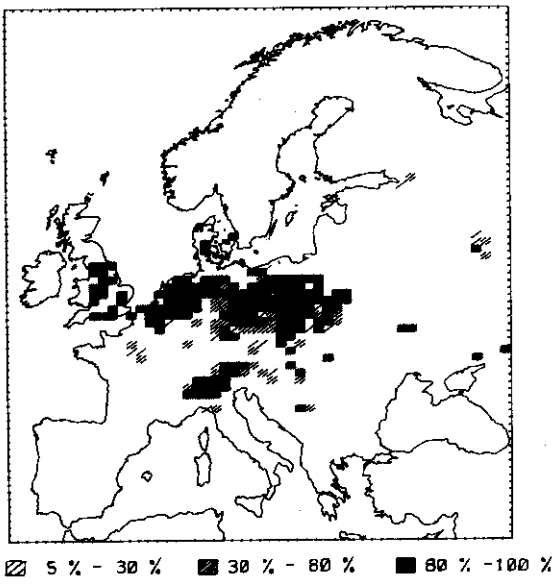

Fig. 7. Model estimates of forest soils below pH 4.2 in 1980. The shading determines the fraction of forest soils below the threshold pH in each grid.

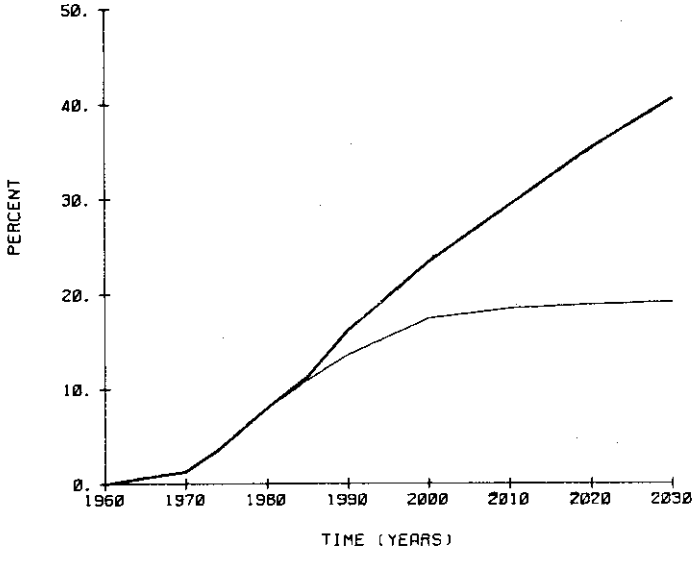

Fig. 8. Time evolution of the total forest area with soils in aluminium and iron buffer range (pH less than 4.2) in Europe assuming the two emission scenarios.

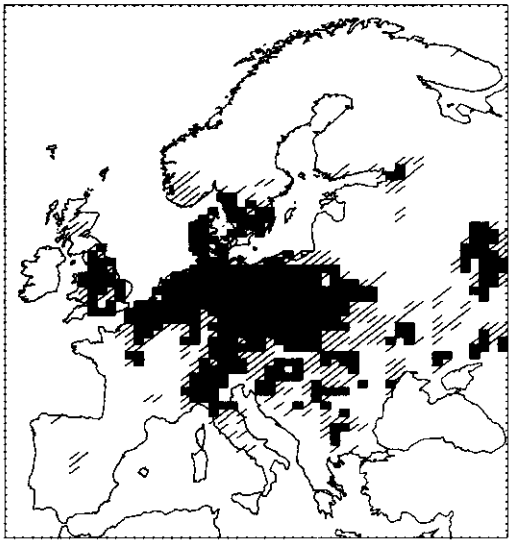

Fig. 9. A comparison of the area at risk in 2010, aluminium and iron being the dominant buffer ranges, resulting from the high emission scenario (light shading) and from the low emission scenario (dark shading).

Central Europe. Continuing with the 'high' deposition scenario the area of low pH substantially enlarges by the year 2010 and much of the soils in Central Europe and Southern Scandinavia reach the aluminium buffer range (Fig. 9).

The region where the soils fall into the aluminium buffer range (pH below 4.2) already appears on the map by 1970. This area, interpreted as the area at risk of forest damage, increases by 1980 (Fig. 7) and, with the 'high' deposition scenario, it is enlarged substantially by the year 2010 (Fig. 9). An option has been added in the computer program for direct comparison of the estimated areas at risk from two scenarios. When the 'low' scenario is used as the input, the results indicate much less risk of forest damage by the year 2010 (Fig. 9). As indicated by Fig. 8 the forest area with soils more acidic than the threshold is estimated to be twice as large with the 'high' scenario as with the 'low' scenario.

DISCUSSION

The model developed in this study can be used for quantifying some aspects of the acidification problem of forest soils previously discussed in only qualitative terms. The soil acidification model and the application to the European overview are simplifications, which necessarily include uncer-

tainties. Many solutions, as they stand now, are crude approximations which need clarification in future research. It is the hope of the authors, however, that the model structure would act as a tool for organizing the data and for identifying research needs. Even in its present stage the model might appear useful in evaluating policies to combat the acidification of forest soils.

The model makes a distinction between reversible and irreversible changes in the soil chemistry. Exhaustion of the buffer capacity is in some cases irreversible. The case of an insufficient buffer rate, in turn, may be reversible: the buffer rate is again sufficient when the stress rate (annual load) is reduced below a threshold which is the value of the buffer rate variable. This feature of the model should be useful as it indicates whether a decrease in the acid stress would result in a recovery of the soil, or whether it would merely cause a delay in the acidification process.

The model, designed for forest soils, appears too complex for agricultural soils. Intensive agriculture maintains high pH values in soils by means of liming and other practices. In theory, the model could be used for calculating, for example, the amount of lime needed to counteract the acidic deposition. This calculation, however, can be done using more straightforward methods.

The application of the model to the problem of acidic deposition in Europe indicates that soil buffering fails to maintain adequate pH levels in large parts of Central Europe. In northern Europe, although the buffering is generally less efficient, the acidic deposition would cause less trouble in this respect. This does not prove that the problem of soil acidification is restricted to Central Europe. Acidification due to biomass accumulation, i.e. the so-called internal proton production, has a special role in northern Europe where low temperatures retard biomass decomposition. High internal proton production increases the susceptibility of the environment to the acidification due to air pollutants. This additional stress needs to be addressed in future research.

The soil variables were initialized for 1960. This does not imply that no acid stress was assumed before that time. The initialization should be viewed as fixing a reference point rather than a manifestation of the state of virgin forests. The initialization should be based on field measurements; in the present application this goal was only partially fulfilled.

The reacting volume was fixed at the top 50 cm of the soil. No horizontal gradients were explicitly assumed. Increasing the reacting volume would postpone the possible problem. Including the gradients would involve faster acidification in the very top of the soil and slower acidification in the deeper layers. The above results correspond to the average situation in the volume. This average value may be inaccurate in some cases due to the nonlinearities of the model.

The model lacks hydrologic considerations since it is only dealing with the uppermost soil layer. However, soil permeability and watershed slope may be important factors in determining the leaching rates of base cations from the soil horizon. Moreover, the model assumes that all deposition actually reacts within the top soil. This may not always be the case. The higher the rate of water input and the coarser the soil texture, the less favourable are the conditions to reach chemical equilibrium between the solutes and the soil matrix. If part of the deposition flows unchanged through the top soil, the soil response will be delayed and the acidification problem is transferred into the adjacent ecosystems or to the groundwater. An effort is currently under way within the IIASA Acid Rain Project to apply the soil acidity model as a component of a regional model of surface water acidification.

Soil acidification poses a threat to forest ecosystems and generates predisposing stress in ecosystems as defined by Manion (1981). Forest damage, however, is a multicausal phenomenon. Many factors are involved such as ozone pollution, heavy metals, exceptional climatic conditions, and cultivation of tree species outside their natural habitats. The interactions of soil acidification and the other factors deserve concerted research effort. It does not seem possible today to describe the forest damage in satisfactory detail with any specific model. But emphasizing the complexity of the forest damage as an argument against serious modelling efforts may well cause a delay in obtaining a better understanding of the phenomenon.

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REFERENCES

Alcamo, J., Hordijk, L., Kämäri, J., Kauppi, P., Posch, M. and Runca, E., 1985. Integrated analysis of acidification in Europe. J. Environ. Manage., 21: 47–61.

Busenberg, E. and Clemency, C.V., 1975. The dissolution kinetics of feldspars at 25°C and atmospheric CO_2 partial pressure. Geochim. Cosmochim. Acta, 40: 41–49.

ECE, 1983. An Efficient Energy Future. Butterworths, London, 259 pp.

Eliassen, A. and Saltbones, J., 1983. Modeling of long-range transport of sulphur over Europe, a two year model run and some model experiments. Atm. Environ., 17: 1457–1473.

Kämäri, J., Posch, M. and Kauppi, L., 1985. Development of a model analyzing surface water acidification on a regional scale: application to individual basins in Southern Finland. In: Proc. Workshop 15–16 September, 1984, Uppsala. NHP Report 10, Nordic Hydrological Programme, Copenhagen, pp. 151–170.

Lammel, R., 1984. Endgültige Ergebnisse und bundesweite Kartierung der Waldschadenserhebung, Allg. Forst Z., 39: 340–344.

Manion, P.D., 1981. Tree Disease Concepts, Prentice-Hall, London, 368 pp.

Matzner, E., 1983. Balances of element fluxes within different ecosystems impacted by acid rain. In: B. Ulrich and J. Pankrath (Editors), Effects of Accumulation of Air Pollutants in Forest Ecosystems. Proc. Workshop, 16–19 May 1982, Göttingen. Reidel, Dordrecht, The Netherlands, pp. 147–155.

Matzner, E. and Ulrich B., 1984. Implications of the chemical soil condition for forest decline. Experimentia (submitted).

OECD, 1979. The OECD programme on long range transport of air pollutants. Measurements and findings. Paris, 164 pp.

Reuss, J.O., 1983. Implications of the calcium–aluminium exchange system for the effect of acid precipitation on soils. J. Environ. Qual., 12: 591–595.

Schütt, P., 1977. Das Tannensterben, Der Stand unseres Wissen über eine aktuelle und gefährliche Komplex-Krankheit der Weisstanne (*Abies alba*). Forstwiss. Zentralbl., 96: 177–186.

Schütt, P., Blaschke, H., Hoque, E., Koch, W., Lang, K.J. and Schuck, H.J., 1983. Erste Ergebnisse einer botanischen Inventur des 'Fichtensterbens'. Forstwiss. Zentralbl., 102: 201–213.

Stumm, W., Furrer, G. and Kunz B., 1983. The role of surface coordination in precipitation and dissolution of mineral phases. Croat. Chim. Acta 56: 593–611.

Ulrich, B., 1981. Theoretische Betrachtungen des Ionenkreislaufs in Waldökosystemen. Z. Pflanzenernähr. Bodenkd., 144: 647–659.

Ulrich, b., 1983a. A concept of forest ecosystem destabilization and of acid deposition as driving force for destabilization. In: B. Ulrich and J. Pankrath (Editors), Effects of Accumulation of Air Pollutants in Forest Ecosystems. Proc. Workshop. 16–19 May 1982, Göttingen. Reidel, Dordrecht, The Netherlands pp. 1–29.

Ulrich., B. 1983b. Soil acidity and its relation to acid deposition. In: B. Ulrich and J. Pankrath (Editors), Effects of Accumulation of Air Pollutants in Forest Ecosystems. Proc. Workshop, 16–19 May, 1982, Göttingen. Reidel, Dordrecht, The Netherlands pp. 127–146.

Ulrich, B., Miewes, K.J., König, N. and Khanna, P.K., 1984. Untersuchungsverfahren und Kriterien zur Bewertung der Versauerung und ihrer Folgen in Waldböden. Forst Holzwirt, 39: 278–286.

Van Breemen, N., Driscoll, C.T. and Mulder, J., 1984. Acidic deposition and internal proton sources in acidification of soils and waters. Nature (London), 307: 599–604.

Wollast, R., 1967. Kinetics of the alteration of K-Feldspar in buffered solutions at low temperatures. Geochim. Cosmochim. Acta, 31: 635–648.

Wright, R.F. and Johannessen, 1980. Input–output budgets of major ions at gauged catchments in Norway. In: D. Drabløs and A. Tollan (Editors). Ecological Impact of Acid Precipitation. Proc. Conf. Sandefjord, Norway, 11–14 March, 1980. SNSF-project, Oslo-Ås, pp. 250–251.

Maps:
FAO-Unesco, *Soil Map of the World*, Vols. I, V. Paris, 1974.
Bundesanstalt für Bodenforschung Hannover, *International Geological Map of Europe and the Mediterranean Region*. Unesco, Paris, 1972.
Weltforstatlas (*World Forestry Altas*), Paul Parey, Hamburg/Berlin, 1975.

APPENDIX

The capacity of the cation exchange buffer system, BC_{CE}^{t}, is depleted with the rate of acid stress, s^t, minus the buffer rate of silicates, br_{Si} (A1). A non-linear relationship is assumed between the base saturation and the soil pH within the silicate, cation exchange and the upper aluminium buffer range, as long as $BC_{CE}^{t} \geqslant 0$, at pH 5.6–4.0 (A2):

$$BC_{CE}^{t} = BC_{CE}^{t-1} - \left(s^t - br_{Si}\right) \tag{A1}$$

$$pH = 4.0 + 1.6\left(BC_{CE}^{t}/CEC_{tot}\right)^{3/4} \tag{A2}$$

The shape of the pH-base saturation relationship has been adopted from results of an equilibrium model by Reuss (1983).

If $BC_{CE}^{t} = 0$, equilibrium with gibbsite is assumed. As precipitation infiltrates into the soil and mixes with the soil solution, disequilibrium concentrations $[Al^{3+}]_s$ and $[H^+]_s$ are obtained (A3, A4):

$$[Al^{3+}]_s = V_f[Al^{3+}]^{t-1}/(V_f + (P - E)) \tag{A3}$$

$$[H^+]_s = \left(V_f[H^+]^{t-1} + \left(s^t - br_{Si}\right)\right)/(V_f + (P - E)) \tag{A4}$$

where V_f is the volume of soil solution at field capacity and P and E mean annual precipitation and evapotranspiration, respectively. On an annual basis the infiltrating water volume is assumed to equal $P - E$. The soil solution volume is simply defined by:

$$V_f = \Theta_f z \tag{A5}$$

The soil thickness, z, is fixed at 50 cm and the volumetric water content value at field capacity, Θ_f is estimated separately for each soil type based on the grain size distribution of the soil. Aluminium is dissolved or precipitated until the gibbsite equilibrium state (A6) is reached.

This process involves a change from disequilibrium concentrations as defined in equation (A7):

$$[Al^{3+}]'/([H^+]')^3 = K_{so}, \quad K_{so} = 10^{+8.5} \tag{A6}$$

$$3([Al^{3+}]_s - [Al^{3+}]') = [H^+]' - [H^+]_s \tag{A7}$$

Combining equations (A6) and (A7) yields a third-order equation which has a single real root (A8):

$$3K_{so}([H^+]')^3 + [H^+]' - 3[Al^{3+}]_s - [H^+]_s = 0 \tag{A8}$$